QUANTITATIVE ANALYSIS OF VARIOUS MATERIALS BY LASER-MICROSPECTROSCOPY

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16. Abstract

    For investigating the possibilities of quantitative laser-microspectroscopy in alloys and in oxidic and sulfidic materials, first tests were carried out with a normal and a Q-switched laser. Calibration curves were determined for the elements: Mg, Al, Ni, Cu, Mo and Ag. Using the relative standard deviation it could be demonstrated, that the determinations obtained with Q-switched laser have more accuracy due to the smaller slope of the calibration curves. Moreover it was ascertained that the reflectivity of metallic samples heavily influences the results obtained with Q-switched and normal laser. Sample inhomogeneities observable microscopically within certain limits only impair the accuracy of the determination, however not making analyses impossible.

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QUANTITATIVE ANALYSIS OF VARIOUS MATERIALS BY
LASER-MICROSPECTROSCOPY

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Introduction

In the now familiar publications on the subject "Quantitative Laser-Micro-spectral Analysis" [1,7] studies only on steel samples were reported. Thus the aim of the present work was to find out on some examples the possibilities for quantitative analysis of other alloys as well as oxidized and sulfidic materials.

To construct the standard curves the laser-microspectral analyzer LMA 1 of the "Jena Optical Works" was used. For each standard series two kinds of standard curves were plotted: one in the unswitched and a second in the Q-switched equipment mode. In this way a simultaneous comparison of the conventional procedure of laser microspectral analysis (without quality control of the resonator) with the so-called Q-switch procedure (with quality control of the laser) was possible in respect to their suitability for quantitative analysis.

In the scope of the experiments, it was meant further to establish how far the inhomogeneity and surface condition of standard and analytical samples influence the accuracy of quantitative laser-microspectral analyses.

Standardization

In order to exclude problems from contaminating elements or third constituents, only binary systems were investigated, impurity level of which fell below 0.1% (a value which is laser-microspectral analysis in a mass of 1 µg for pure elements is the relative limit of detection [8,9]).

In Table 1 are those materials in which a determination of the components named above was intended. To set calibrating concentration ranges, the

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*Numbers in the margin indicate pagination in the foreign text.

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approximate concentrations of the elements to be assayed were determined in pre-
liminary tests. Further, tests were made to determine whether these concentra-
tions in all cases were above the quantitative limits of detection also esta-
blished in the tests for these elements (which don't have to be absolutely
identical in their detection limits).

TABLE 1. SUMMARY OF THE ANALYTICAL MATERIALS PROVIDED
IN THIS WORK FOR QUANTITATIVE DETERMINATION

Alloys	Oxides	Sulfides
Ag/Cu	Ag_2O/CuO	Ag_2S/Cu_2S
Ni/Cu	MgO/Bi_2O_3	MoS_2/Cu_2S
Al/Zn		
Cu/Ag		

Preparation of the various kinds of standard samples is reported in detail
in the following:

a) Metallic Standard Samples

The makeup of the total of four metallic standard series yielded for the
elements Ag, Ni, Al and Cu the concentration ranges entered in Table 2, column 3.

TABLE 2. CONCENTRATIONS OF THE STANDARD SAMPLES USED (COLUMN
3) AND WAVELENGTHS (COLUMN 4) OF THE ELEMENT LINES USED FOR
SPECTRAL EVALUATION

Column 1	Column 2	Column 3	Column 4
Standard material	Alloying element/ Matrix element	Concentration of standard samples (Wt -%) (rel. error<1%)	Wavelengths of the spectral lines evaluated (nm)
Alloys	Ag/Cu	5,5; 7,5; 9,9; 14,1; 19,5	Ag: 338,29; Cu: 327,40
	Ni/Cu	2,1; 5,3; 10,5; 15,2; 20,0	Ni: 341,48; Cu: 327,40
	Al/Zn	0,52; 0,73; 0,99; 2,45; 3,55; 4,9	Al: 308,23; Zn: 328,23
	Cu/Ag	1,2; 4,7; 7,6; 9,7; 14,9; 19,4	Cu: 327,40; Ag: 338,29
Oxides	Ag_2O/CuO	1,1[a]; 5,0; 7,2[b]; 10,6; 15,5; 20,5	Ag: 338,29; Cu: 327,40 Ag: 244,79
	MgO/Bi_2O_3	0,1; 0,5; 0,76; 1,05; 2,55; 5,1; 7,45; 10,0; 12,4	Mg: 279,08; Bi: 289,78
Sulfides	Ag_2S/Cu_2S	4,9; 7,5; 10,3; 14,8; 20,0	Ag: 243,78; Cu: 296,12
	MoS_2/Cu_2S	1,04; 2,5; 5,2; 7,6; 10,1	Mo: 281,62; Cu: 327,40 Mo: 287,15; Cu: 254.48

[a]Only for measuring without Q-switch; [b] only for the tests with
Q-switch.
Commas indicate decimal points.

The required 22 standard alloys were made in quartz crucibles by intensive fusion of appropriate amounts of the elements functioning as base material and elements to be analyzed in the inert gas medium argon.

Since material losses by vaporization of one of the two components were not excluded in this, all samples after melting were subjected to chemical analysis to determine the precise concentrations of the alloying elements. The values found (relative error < 1%) can be taken from column 3 of Table 2.

From each melt, two polished, ground specimens were prepared, one of which was again roughened with SiC (grain size 30-40 μm). Both types of section were used as test samples.

b) Oxidic and Sulfidic Standard Samples

The standard samples of the oxidic and sulfidic standard series (concentration range see Table 2, column 3) first were prepared in the form of powder mixtures, which, by internal mixing of the oxide or sulfide, has become extensively homogenized by matrix and alloying elements.

But since laser microspectral analyses could not be undertaken on powdery substances, these mixtures had to be converted into compact test samples. The various powders therefore were compressed under a pressure of 600 kPa (6 at) into tablets (1.5 cm thick). The sulfidic compresses already showed such notable hardness that attendant sintering could be disregarded.

The oxidic tablets, on the other hand, had to be hardened by 7 hour sintering at some 200 K below the melting point of the respective matrix oxides. For each standard sample, a density measurement was made with the aid of a precision balance with a hydrostatic device, to provide values for the later calculations /23 [4] of the masses vaporized by the laser beam.

Analytical Apparatus

Much already has been reported about the construction and function of the conventional LMA 1 [5,8], so that no more of that shall be discussed here. Let us merely emphasize that in this apparatus, with the aid of a Nd-glass resonator, a laser radiation of 1060 nm wavelength is produced, which is emitted as an impulse of 0.2 μsec duration and a maximum energy of 1 Ws. This radiation is

unregulated radiation that is composed of numerous statistically consecutive spikes of various peak outputs and time intervals.

If one extends the usual laser-microspectral analyzer by the so-called Q-switch auxiliary, then one gets emission of several spikes fewer of uniform peak output.

In incorporating this auxiliary, the following changes are undertaken in the structure of the resonator head:

In place of the Nd-glass rod, there is a ruby rod with plane-parallel faces, and thus, without the metallized end surfaces usual in the former and without the reflecting roof-edge prism. Instead, an output mirror was mounted between ruby and rotating mirror of the laser beam to the microscope. On the other side of the ruby, a cuvette for the switching liquid was placed with a totally reflecting prism.

The switching liquid consisted of methanol or acetonitrile and a cyanine dye, e.g., crypto- or phthalocyanine. This dissolved dye, during the laser's pumping process under the influence of the increasing number of light quanta in the resonator, loses its absorbing power within a few nanoseconds, and the whole inversion built up till then is degraded in an enormous impulse with an extremely short half-life and thus high peak output, if the concentration of the switching dye is high enough.

With inferior dye concentrations, the switching process recurs often during a pumping impulse of the flash lamp, and several giant impulses occur with correspondingly lower peak outputs.

The transmittance T of the switching solution at a wavelength of 693 nm serves as a measure for the dye concentration and thereby for the number of giant impulses produced per flash lamp impulse. From the experiments of Moenke-Blankenburg and Mohr [6], a single giant impulse should be expected at a transmittance of 55%; 3-20 giant impulses occur at T = 75-95%.

Research Conditions

For the present studies the laser microspectral analyzer was combined with the Q24 prism spectrograph (Zeiss, Jena). The spectra were taken on Orwo-WU2 spectral plates.

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The energy of the laser radiation in all tests, both with and without Q-switching of the LMA 1, was so adjusted that 5 µg of material could be vaporized. Such a weighed portion, which is calculated from the crater measurements [4], is the least necessary to yield good evaluable spectra. Besides, the transmittance of the switching solutions used in Q-switch operations may not amount to less than 85-89%. The value of 89% should never be exceeded because that would have led to poorer reproducibility of the material evaporation.

Discharge-capacity and -inductivity of the spark discharge necessary for cross excitation were chosen according to experience from earlier work [8, 9].

Further technical data are summarized in Table 3.

TABLE 3. VALID TECHNICAL DATA FOR THE QUANTITATIVE
LASER-MICROSPECTRAL ANALYSIS WITH AND WITHOUT Q-SWITCHING
ACCORDING TO OUR EXPERIENCES

Collimator setting on the Q24	9.9 drum divisions
Dispersion and slit width on the Q24	1.35 nm/mm; 15 µm
Microscope objective on the LMA 1	Mirror objective 40 x 0.5 Focal length 6.3 mm Working distance 15.8 mm
Ocular magnification	12.5 X
Maximum starting energy of the laser	
Uncontrolled	
In operation	1 Ws
Switching solution (SS)	Cryptocyanine[a]/acetonitrile
Transmittance of the SS	T = 85-89% (according to material)
Number of giant impulses at T = 85-89%	8-10
Output energy at T = 85-89%	220-225 mWs
Excitation voltage	3.0 kV
Discharge inductivities and capacities	L:500 µH; C:1.5 µF or L: 60 µH; C:2.0 µF
Development of the Orwo-WU2 spectral plates	Tetanal-Metolhydroquinone diluted 1:5, 4 min, rocking development at 18°C
Evaluating instrument	Rapid photometer GII of the Jena Optical Works

[a] $C_{25}H_{25}N_2I$ — 1.1'-diethyl-4.4'-carbocyanine iodide.

Evaluation

In column 4 of Table 2 are the wavelengths of the element lines used to evaluate the various materials.

With consideration of the background blackening, first the line intensities of matrix and alloying elements were determined, and then the intensity ratios were calculated from these values and were plotted in Figures 1-8 as function of the standard concentrations. The curves on the left side of these diagrams apply to runs with the unswitched, those on the right side to those with Q-switched laser operation.

a) Metallic Standard Curves

All useful standard curves of Figures 1-4 of alloys suitable for analysis are the result of researches on the above-mentioned roughed metal sections. While the construction of standard curves turned out relatively frictionless by means of Q-switched laser radiation, in the unswitched laser operation, because of the excessive fluctuation of the measured values, it was impossible to plot standard curves for the Ni/Cu and Al/Zn alloys. Hence the lack of such curves in Figures 2 and 3.
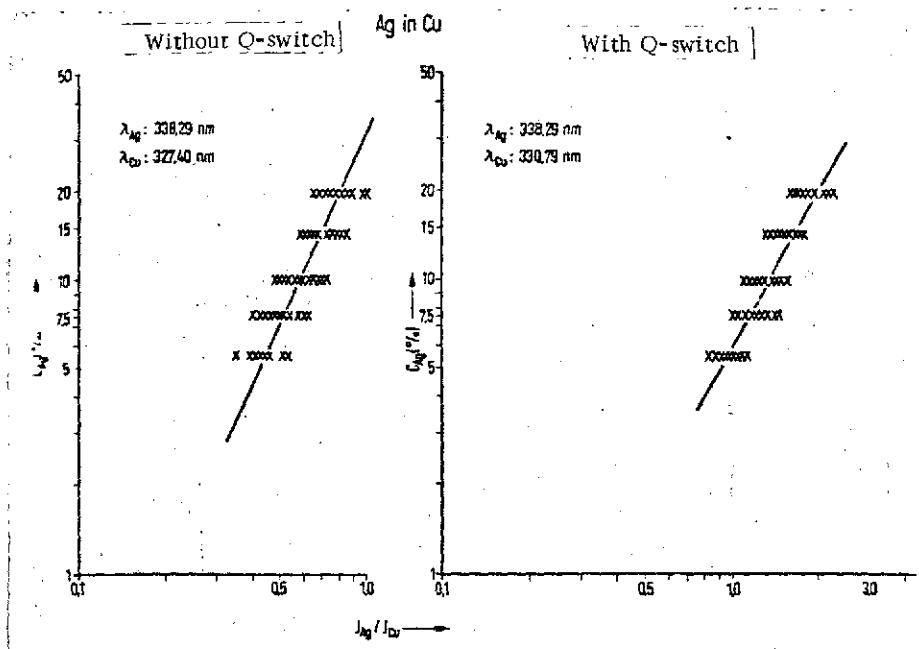

Figure 1. Standard Curves for the Quantitative Laser-Microspectral Analysis of Ag/Cu Allows Withoand Without Q-Switch Auxiliary.
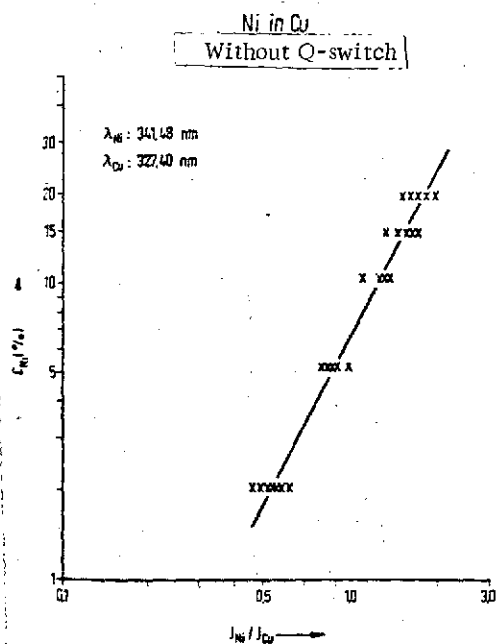
Figure 2. Standard Curves for the
Quantitative Laser-Microspectral
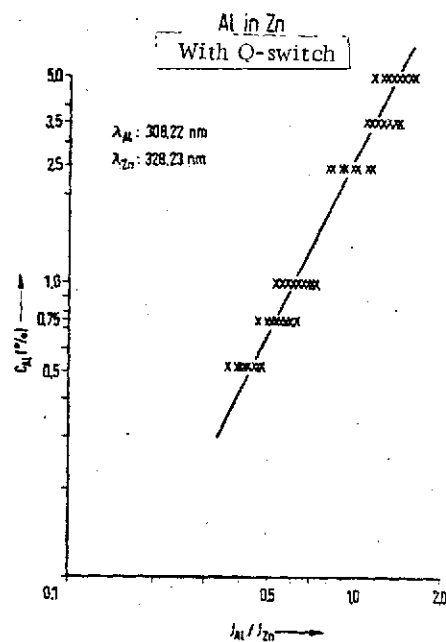Analysis of Ni/Cu Alloys with Q-
-Switch.

Figure 3. Standard Curves for the
Quantitative Laser-Microspectral
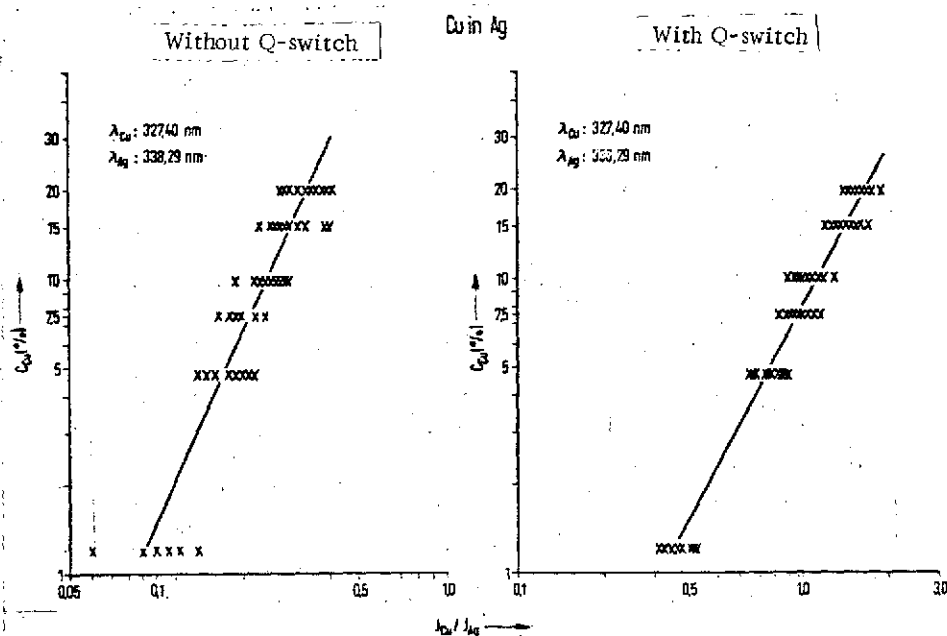Analysis of Al/Zn Alloys with Q-
-Switch.

Figure 4. Standard Curves for the Quantitative
Laser-Microspectral Analysis of Cu/Ag Alloys
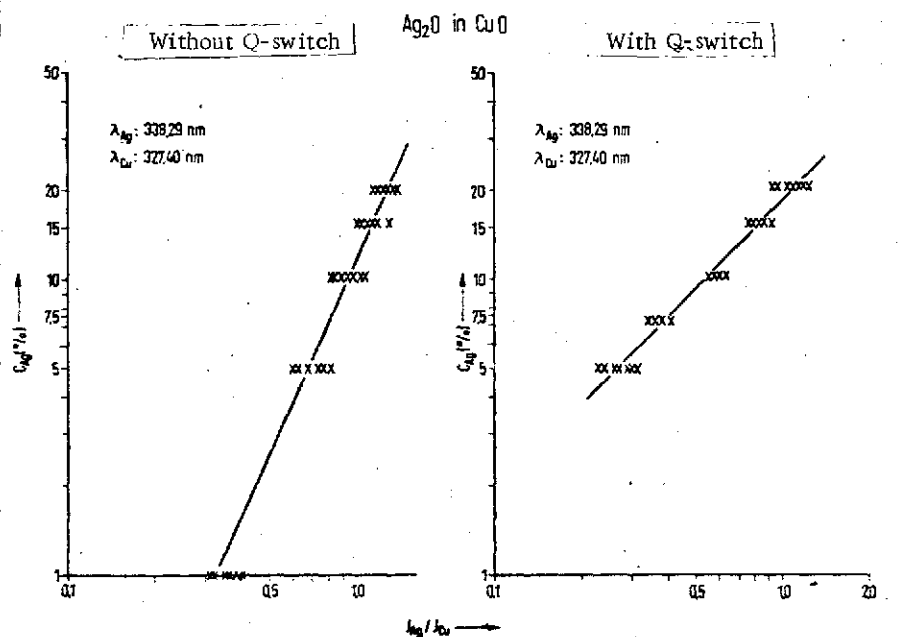with and without Q-Switch.

Figure 5. Standard Curves for the Quantitative Laser-Microspectral Analysis of Ag_2O/CuO Samples with and without Q-Switch.

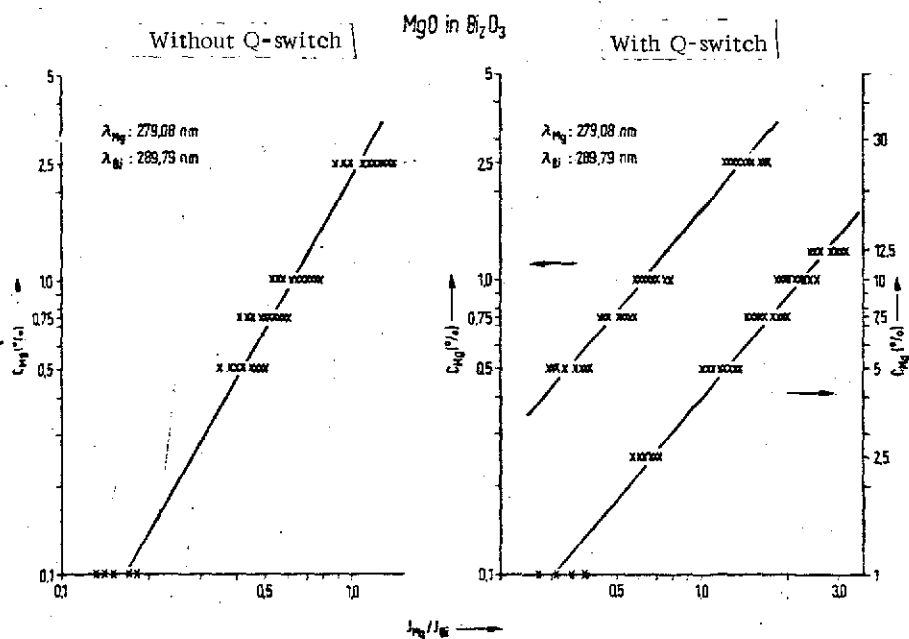

Figure 6. Standard Curves for the Quantitative Laser-Microspectral Analysis of MgO/Bi_2O_3 Samples with and without Q-Switch.
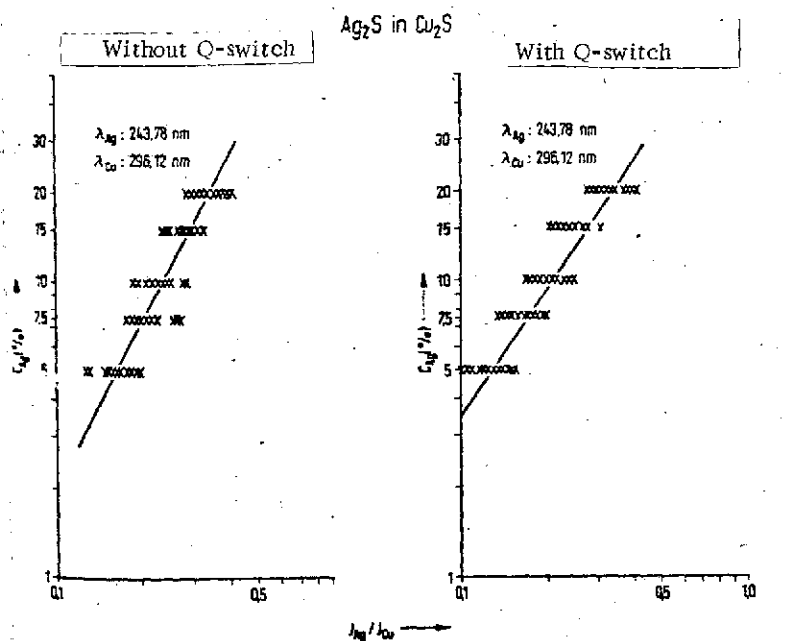
Figure 7.   Standard Curves for the Quantitative Laser-Microspectral Analysis of Ag_2S/Cu_2S Samples with and without Q-Switch.
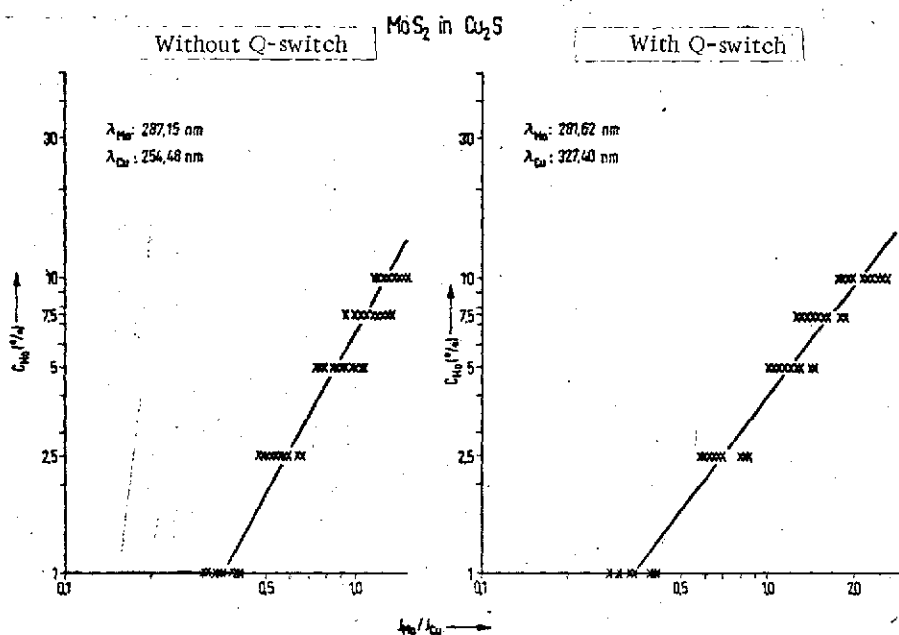

Figure 8.   Standard Curves for the Quantitative Laser-Microspectral Analysis of MoS_2/Cu_2S Samples with and without Q-Switch.

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In working without Q-switch, then, a standardization can be questioned under certain circumstances. Thus in the analysis of metals, investigations in Q-switched operations are preferred over those without Q-switch.

All attempts to construct standard curves with use of the polished sections were fruitless because of the excessive scattering of the measured values. Since these considerable fluctuations appeared not only in studies in unswitched, but even in the switched laser work to a great extent, one finally stopped using polished specimens in general.

Polished and roughened sections come from the same melt regulus. They therefore differ neither in composition nor structure, but only in the condition of their surfaces and so in their reflectivities. Accordingly it also must be /25 assumed that only this higher reflectivity of the polished samples is to be considered responsible for disturbances which occur.

As can be seen from the phase diagrams [2] of the alloys considered here, only the standard samples of the Ni/Cu series are obtained in the form on monophasic melt products. All the other alloys occur as multiphasic products, thus are microscopically more or less inhomogeneous.

Because of these inhomogeneities, the curves of these alloys indeed exhibit a broader scatter than those of the Ni/Cu series, but does not impede quantitative analyses.

b) Standard Curves of Oxides and Sulfides /26

The standard curves for the analysis of oxidic and sulfidic materials are rendered in Figures 5-6 and 7-8, respectively. Those for Q-switched laser operation again appear on the right side of the diagram.

Considerable scattering occurs to nearly equal extent in the curves made both without and with Q-switch. The inhomogeneity of the test samples can be regarded as at least partially responsible.

As in slight degree in the studies on alloys (see Table 4, column 3), here too a difference in the slope of standard curves obtained in unswitched and Q-switched procedures is noted (see column 3, Table 4). Especially great is the difference in the slopes of the Ag_2O/CuO curves.

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TABLE 4. SLOPES OF THE STANDARD CURVES OF UNSWITCHED
9oQ) AND Q-SWITCHED (mQ) LASER OPERATION AS WELL AS RELATIVE
STANDARD DEVIATIONS s_1(oQ), s_2(mQ) AND THE QUOTIENTS

$Q = s_1/s_2$ (NUMBER OF MEASURED VALUES N = 25)

CALCULATED FROM THESE

Column 1	Column 2	Column 3		Column 4		Column 5
Standard material	Alloying element/ Matrix element	Slope of standard curves		Relative standard deviations		s_1/s_2
		a) oQ	b) mQ	a) s_1(oQ)	b) s_2(mQ)	
Alloys	Ag/Cu	2,15	1,80	0,26	0,16	1,63
	Ni/Cu		1,88		0,15	
	Al/Zn		1,96		0,16	
	Cu/Ag	2,15	1,80	0,28	0,14	2,00
Oxides	Ag₂O/CuO	2,15	1,00	0,17	0,07	2,40
	MgO/Bi₂O₃	1,73	1,15	0,20	0,10	2,00
Sulfides	Ag₂S/Cu₂S	1,88	1,43	0,23	0,16	1,44
	MoS₂/Cu₂S	1,88	1,28	0,18	0,12	1,50

Commas indicate decimal points.

The flattening of the curves by working in the Q-switch mode may work to
advantage in obtaining better accuracy of the concentration determinations
made with them.

Evaluation of the Results

To define the accuracy of a measuring process, one makes use in the analysis,
among other things, of the "relative standard deviation". For the present
research series, this relative standard deviation is calculated according to
the Kaiser and Specker [3] formula. The values found are in column 4 of Table
4 and are differentiated for studies in the unswitched (s_1) and switched (s_2)
laser work.

In all three kinds of material, the (deviation) values of the work done
without Q-switch are considerably above those with Q-switch.

A simple comparison of the standard deviations, however, allow no decision
as to whether the Q-switch process actually is the better procedure.

But the following consideration yields this decision:

The difference of the standar deviations s_1 and s_2 ($s_1 > s_2$) is considered as statistically certain according to [3], when

The proof quantity Q depends on three parameters, the required certainty S, and the numbers N_1 and N_2 of the measurements on which calculation of the standard deviation is based.

For 25 measurements ($N_1 = N_2$), the difference of the measuring processes to be compared is certified to S = 95, 99 or 99.7% respectively, when the quotient amounts to Q = 1.41, 1.63 or 1.80.

With exception of the Ni/Cu and Al/Zn series, for all other standards series the calculated quotients s_1/s_2 are recorded in column 5 of Table 4. There all the quotients exceed the least value of 1.41 (S = 95%). In all cases therefore there is a true difference between the two procedures. This shows the better adaptation of the Q-switch process as an analytical procedure for the materials investigated here. That holds for the studies on oxides and Cu/Ag alloys with absolute, for those on Ag/Cu alloys with 99%, for those on sulfides with 95% certainty.

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